

**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH**

**ANNUAL TECHNICAL REPORT**

for

Contract Number F49620-93-1-0110

**PHOTOFRAGMENTATION SPECTROSCOPY AND  
PHOTODISSOCIATION DYNAMICS OF POLYATOMIC MOLECULES**

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January 31, 1994

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# REPORT DOCUMENTATION PAGE *Dist: A*

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Weiner, Brad R.		Principal Investigator		[Signature]		1994/10/12		1994/10/12		1994/10/12	

distributions have been measured from rovibronically resolved spectra to support our discussion on the detailed dissociation mechanism. Quantum yield measurements suggest that other electronic states of the SO radical may be directly produced. This work is being prepared for publication in *Chemical Physics*.

### $(\text{CH}_3)_2\text{SO}$

The photodissociation dynamics of the reaction,  $(\text{CH}_3)_2\text{SO} + h\nu(193 \text{ nm}) \rightarrow 2\text{CH}_3 + \text{SO}$ , have been examined by laser spectroscopic techniques. Relative vibrational and rotational state energy distributions of the nascent SO photofragment have been determined by using laser induced fluorescence spectroscopy on the  $(\text{B}^3\Sigma^- - \text{X}^3\Sigma^-)$  transition. The same technique has also been employed to establish the quantum yield,  $\Phi_{193}[\text{SO}(\text{X}^3\Sigma^-)] = 1.02 \pm 0.12$ . The nascent vibrational state distributions in the  $\nu_1$  and  $\nu_2$  modes of the methyl radical have been determined by using 2+1 resonance enhanced multiphoton ionization spectroscopy via the  $(3p \ ^2\text{A}_2'' \leftarrow 2p \ ^2\text{A}_2'')$  transition. These measurements were done in collaboration with M. Hawley and H.H. Nelson at the Naval Research Laboratory.

The energy distributions of the nascent fragments are best described by a concerted three-body fragmentation. While some of our data are suggestive of a concerted synchronous dissociation of the two S-C bonds in DMSO,<sup>2</sup> we cannot conclusively determine the synchronicity from our results. Further studies of the photofragment angular distributions following 193 nm irradiation of dimethyl sulfoxide would be helpful in analyzing this aspect of the dissociation dynamics. This work has been published in the *Journal of Physical Chemistry* (see publication).

### $\text{C}_6\text{H}_5\text{NSO}$

The photodissociation dynamics of the reaction,  $\text{C}_6\text{H}_5\text{NSO} + h\nu(193 \text{ or } 248 \text{ nm}) \rightarrow \text{C}_6\text{H}_5\text{N} + \text{SO}$ , have been examined by laser spectroscopic techniques. Relative vibrational and rotational state energy distributions of the nascent SO photofragment have been determined by using laser induced fluorescence spectroscopy on the  $(\text{B}^3\Sigma^- - \text{X}^3\Sigma^-)$  transition. The vibrational distribution has been found to be inverted with a maximum at  $V''=1$ . We have also tried to spectroscopically characterize the other fragment, which is expected to be phenylnitrene. We began our characterization by searching in the 500 nm region for a laser induced fluorescent signal based on theoretical studies. A signal was obtained, but was unable to be characterized as the ground state of phenylnitrene. Through a collaboration with Professor J.M. Hossenlopp (Department of Chemistry, Marquette University), we now believe the carrier of this spectroscopic signal to be Dehydroazepine, which is the wing expanded isomer of the Phenylnitrene. Work is in progress now to fully characterize these species. This work is being prepared for *Journal Physical Chemistry*.

The experiments involving  $\text{SO}(\text{X}^3\Sigma^-)$  remain a target of this proposed research, and are extremely valuable to the Air Force because of the atmospheric importance of these species. Along a similar line, we have studied the reaction dynamics of the vinoxy ( $\text{C}_2\text{H}_3\text{O}$ ) radical. The

primary motivation for this study was that it was a species of interest, and that it provided a nice vehicle for training new graduate students to use the experimental apparatus. Some of this work has been published in *Chemical Physics Letters*, as a result of our first grant proposal with AFOSR (F49620-89-C-0070). We have now discovered a whole new phase of this research, which we believe is consistent with this project, and that we are now pursuing.

### $C_2H_3O$

State specific radiative lifetimes and electronic quenching cross-sections have been determined for three different vibrational modes of  $C_2H_3O$  ( $\tilde{B}^2A''$ ). These experiments were carried out using a two-laser method with laser-induced fluorescence as the detection technique. Ground state vinoxy radicals were produced by 193nm excimer laser photolysis of  $CH_3OCH=CH_2$ , and were pumped to the B state by a tunable dye laser. Fluorescence decay rates were determined in the presence to ten collision partners: He, Ar,  $N_2$ ,  $O_2$ , CO,  $H_2$ , HCl,  $CO_2$ ,  $C_2H_4$ , and  $CH_3OCH=CH_2$ . The measured electronic quenching cross-sections vary from 0.01 - 66.5  $\text{\AA}^2$ . A vibrational level dependence was found for the radiative lifetimes, which is believed to be due to predissociation. We are now investigating the photodissociation of the vinoxy radical at 308 nm. In particular we believe that the primary photoproducts of 308 nm photolysis of vinoxy are  $CH_2$  and HCO. We will begin these studies by searching for formyl radical by LIF spectroscopy. This work is being prepared for publication.

### III. PUBLICATIONS

Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner, "UV Photochemistry of Thionyl Aniline", *Manuscript in Preparation*.

Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner, "Rotational Distributions of  $SO(X^3\Sigma)$  from the 193 and 210 nm Photodissociation of  $SO_2$ ." J. Chem. Phys. *To be submitted*.

Katherine I. Barnhard, Min He and Brad R. Weiner, "Fluorescence Lifetimes of  $C_2H_3O(B^2A')$ : Evidence for Predissociation." J. Phys. Chem. *To be submitted*.

Hongxin Wang, Xirong Chen, and Brad R. Weiner, "Photodissociation Dynamics of Thionyl Bromide at 193 and 248 nm" Chem. Phys. *To be submitted*.

Hongxin Wang, Xirong Chen and Brad R. Weiner, " $SO(X^3\Sigma)$  Production from the 193 nm Laser Photolysis of Thionyl Fluoride", Chem. Phys. Lett. 216, 1993, 537.

Xirong Chen, Hongxin Wang, Brad R. Weiner, Michael Hawley and H.H. Nelson, "Photodissociation of Dimethyl Sulfoxide at 193 nm in the Gas Phase", J. Phys. Chem. 97, 1993, 12269.

Hongxin Wang, Xirong Chen, and Brad R. Weiner, "*Laser Photodissociation Dynamics of Thionyl Chloride: Concerted and Stepwise Cleavage of S-Cl Bonds*", J. Phys. Chem. 97, 1993, 12260.

Xiaotian Gu, Luis A. Muñoz, Yasuyuki Ishikawa, and Brad R. Weiner, "Isotope Effects and Wavelength Dependence in the Rotational State Distributions of the Diatomic Photofragments, SH and SD, from the Photodissociation of  $H_2S$  and  $D_2S$ ", Chem. Phys. Lett. 211, 1993, 65.

### IV. PERSONNEL

#### Senior Personnel

Professor Xirong Chen from the Dalian Institute of Chemical Physics, Dalian, P.R. China, joined our research group in February, 1990.

#### Junior Personnel

Hongxin Wang (Ph.D. granted May 1993, Chemical Physics Program)

Katherine I. Barnhard de Sanfiorenzo (Ph.D candidate, Department of Chemistry)

Fei Wu (Ph.D. Candidate; Chemical Physics Program)  
Stephen Gomez (Undergraduate student, Department of Chemistry)

## V. PRESENTATIONS

### International

"Photochemistry of Thionyl Bromide at 193 and 248 nm in the Gas Phase"

Hongxin Wang, Xirong Chen and Brad R. Weiner

XVI<sup>th</sup> International Conference on Photochemistry, Vancouver, BC, Canada, 1-6 August 1993.

"Structure and Spectroscopic Properties of the Photofragment, ClSO Radical and Its Isomer, ClOS, in the Ground <sup>2</sup>A" State"

Gustavo E. Lopez, Brad R. Weiner and Yasuyuki Ishikawa

XVI<sup>th</sup> International Conference on Photochemistry, Vancouver, BC, Canada, 1-6 August 1993.

"Three Body Photodissociation of Thionyl Chloride"

Xirong Chen, Hongxin Wang and Brad R. Weiner

1993 Conference on the Dynamics of Molecular Collisions, Helen, Georgia, 6-11 June 1993.

"The Photochemistry of Thionylaniline"

K. Matos, X. Chen, H. Wang, and Brad R. Weiner

205th National Meeting of the American Chemical Society, Denver, Colorado, 29 March - 2 April 1993.

"Synthesis, Characterization and Photochemistry of Mixed Metal Clusters"

E. Meléndez, A. Gonzalez, R. Delgado, M.M. Muir and Brad R. Weiner

205th National Meeting of the American Chemical Society, Denver, Colorado, 29 March - 2 April 1993.

### Regional

"Flash Photolysis of Low Nuclearity Metal Clusters"

Stephen Gómez, Ruben Delgado, Takahiro Yabe and Brad R. Weiner

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993



"Nascent  $\text{SO}(\text{X}^3\Sigma^-)$  Vibrational, Rotational and Spin State Distributions from the 193 nm Photodissociation of  $\text{SO}_2$ "

Fei Wu, Xirong Chen, Yasuyuki Ishikawa and Brad R. Weiner

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993

" $\text{SO}(\text{X}^3\Sigma^-)$  Production from the 193 nm Laser Photolysis of Thionyl Fluoride"

Hongxin Wang, Xirong Chen and Brad R. Weiner

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.

"Ab Initio Hartree-Fock and CAS MC SCF Calculations on the Ground  $^2\text{A}$ " and Excited  $^2\text{A}'$  State Potential Energy Surfaces"

Vijaya Keshari, Brad R. Weiner and Yasuyuki Ishikawa

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.

"The Photochemistry of Thionylaniline"

Brad R. Weiner

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.

"Multiphoton Ionization Spectrum of  $\text{SOCl}_2$  in a Supersonic Jet"

Manuel A. Rivera, T. Yabe and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993

"Vibrational Relaxation of Sulfur Monoxide Radicals at 298K"

Félix M. Martínez, Xiaotian Gu and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993

"Photochemistry of Low Nuclearity Metal Clusters"

R. Delgado, E. Meléndez, T. Yabe and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993.

## Universities

"Dynamics of Sulfur Monoxide Photoelimination Reactions" (invited)

Brad R. Weiner

Department of Chemistry, Marquette University, Milwaukee, Wisconsin, 10 November 1993

"Dynamics of Sulfur Monoxide Photoelimination Reactions" (invited)

Brad R. Weiner

Molecular Physics Division, National Institute of Standards and Technology,

Gaithersburg, Maryland, 6 October 1993

"Dynamics of Sulfur Monoxide Photoelimination Reactions"

Brad R. Weiner

Department of Chemistry, Tulane University, New Orleans, Louisiana, 1 February 1993

## VI. INTERACTIONS

The dimethyl fulfoxide studies were carried out in conjunction with M. Hawley and H. Nelson at the Naval Research Laboratory. We have also initiated a collaboration with D. King and co-workers at NIST, to study the photodissociation dynamics of HNSO. This is partially motivated by an undergraduate student from my lab who did a summer internship at NIST. We have an active collaboration in the thionylaniline experiments with J. Hossenlopp at Marquette University, whose studying these reactions by infrared absorption methods.

## VII. SUMMARY

An active program in state-resolved photochemistry is ongoing in the Department of Chemistry at the University of Puerto Rico-Río Piedras. The detailed mechanisms of polyatomic photodissociation processes can be revealed by measurement of the nascent rotational and vibrational state distributions of one or more of the photofragments following photoactivation. Photodissociation of  $\text{SO}_2$ ,  $\text{X}_2\text{SO}$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}$  or  $\text{CH}_3$ ) and  $\text{C}_6\text{H}_5\text{NSO}$  have been shown to produce ground state sulfur monoxide following 193 nm (and in some cases 248 nm) photofragmentation. The nascent vibrational and rotational energy distributions of the SO photoproduct from all the parent molecules have been measured by laser induced fluorescence on the B-X transition in the wavelenth region of 240-290 nm. The nascent rotational distributions have been measured for  $\text{SO}(\text{X}^3\Sigma^-, v''=1,2,3)$ . The results indicate that for 193 nm photolysis of thionyl chloride, thionyl bromide and dimethyl sulfoxide, a concerted three-body fragmentation process is occurring, while a stepwise process occurs in the 248 nm photodissociation of  $\text{Cl}_2\text{SO}$ . The work is now being extended to cyclic sulfoxides.